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Soil chemical and fertilizer influences on soluble and medium-sized colloidal phosphorus in agricultural soils

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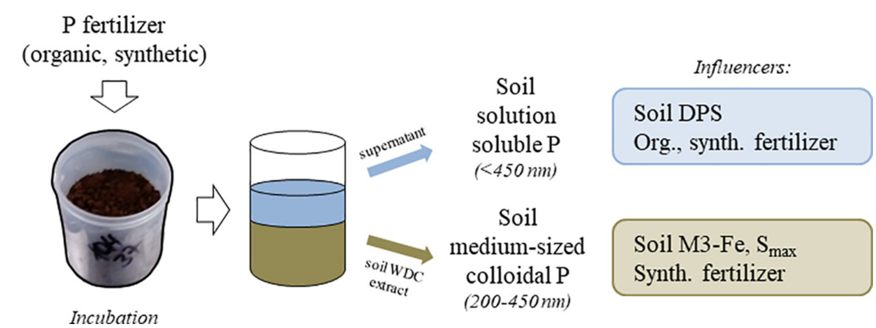
HIGHLIGHTS

- Medium-sized (200–450 nm) soil colloidal and soluble soil solution P were analysed.
- Amorphous forms of Fe increased the major fraction of medium-sized colloidal P.
- Soil S_{max} and DPS influenced medium-sized colloidal P and soluble P, respectively.
- Cattle slurry did not influence medium-sized colloidal P but increased soluble P.
- Synthetic fertilizer influenced medium-sized colloidal P and increased soluble P.

GRAPHICAL ABSTRACT



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ABSTRACT

Colloid-facilitated transport can be important for preferential transfer of phosphorus (P) through the soil profile to groundwater and may in part explain elevated P concentrations in surface water during baseflow and particularly high flow conditions. To investigate the potential for colloidal P (P_{coll}) mobilisation in soils, this study assessed the role of soil chemical properties and P fertilizer type on medium-sized soil P_{coll} (200–450 nm) and its association with soil solution soluble bioavailable P (<450 nm). Hillslope soils from three agricultural catchments were sampled and untreated and treated (cattle slurry and synthetic fertilizer) subsamples were incubated. Soil supernatants were analysed for P and soil Water Dispersible Colloids (WDC) were extracted for analysis of P and P-binding materials. Soils physicochemical properties including degree of P saturation (DPS) and P sorption properties were determined. Results indicated that medium-sized P_{coll} was mostly unreactive P associated to some extent to amorphous forms of Fe. Medium-sized P_{coll} concentrations correlated negatively with soil maximum P sorption capacity and soluble P concentrations increased with increasing DPS. In soil with low sorption properties, cattle slurry increased soluble P concentrations by 0.008–0.013 mg l^{-1} and DPS but did not influence medium-sized P_{coll}. Synthetic fertilizer increased medium-sized reactive P_{coll} by 0.011 mg l^{-1} (0.088 mg kg^{-1} soil) and DPS in a soil with lower DPS whereas it decreased it by 0.005 mg l^{-1} (0.040 mg kg^{-1} soil) in a soil with higher DPS. Additional soil parameters (M3-Fe, M3-Al, M3-P, and DPS) should be included in soil testing, especially in Cambisol/Podzol soils, to identify critical areas where risks of P_{coll} mobilisation are important. Further research should include the roles of finer colloidal and nanoparticulate (<200 nm) soil P fractions and soluble P to inform understanding of plant uptake and assess environmental risk.

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1. Introduction

Phosphorus (P) is a key nutrient for global food production (Némery and Garnier, 2016) but losses from agricultural soils into water bodies can lead to ecological issues caused by eutrophication (Andersen et al., 2017). A range of P species can be found in water (Van Moorleghem et al., 2011) such as inorganic phosphate directly bioavailable in its dissolved form (Ekholm, 1994) or organic esters of phosphoric acid (Turner et al., 2005). Phosphate can also be present as colloidal phosphate precipitates, or associated with colloidal clay and metal oxide particles and become bioavailable after its release by dissolution or desorption, respectively (Jeanneau et al., 2014; Lambert et al., 2013), or by diffusion near the plant root (Montalvo et al., 2015). However, some studies suggest that some colloidal P (P_{coll}) forms could be directly bioavailable (Van Moorleghem et al., 2013). Colloids present higher specific surface areas for P binding compared to bulk soil, are mobile in soil, remain in solution for long periods of time (Baalousha et al., 2005) and may thus be important for preferential transfer of nutrients and contaminants (Jiang et al., 2015; Missong et al., 2016) through the soil profile to groundwater (GW).

Colloidal P mobilisation in soils can depend on chemical drivers, including anoxia (Henderson et al., 2012), degree of P saturation (DPS) (Ilg et al., 2008; Siemens et al., 2004), pH (Séquaris et al., 2013) and ionic strength (Rousseau et al., 2004). Other reported dependencies include management-related drivers such as fertilizer rate of application (Zhang et al., 2003), fertilizer type (Heathwaite et al., 2005; Ilg et al., 2008) or ploughing of tillage soils (Schelde et al., 2006), and physical drivers such as rainfall rate (Rousseau et al., 2004), soil moisture (Jiang et al., 2013; Mohanty et al., 2015) and temperature (Jiang et al., 2017). Organic acids (contained in soils and animal slurry, for example) can also compete with phosphate for the same colloidal sorption sites via ligand exchange or solubilize phosphate via ligand promoted mineral dissolution (Oburger et al., 2011). This may alter the association between mobile soil P_{coll} and P that is dissolved and more easily bioavailable.

Groundwater pathway connectivity is important for P transfers and there is increasing evidence that GW P is a concern for stream water quality (Dupas et al., 2017; Mellander et al., 2016). While stream-bed and karst remobilisation of P (Hongthanat et al., 2016; Jarvie et al., 2014), P release from wetlands (Dupas et al., 2015), and rural point sources (Withers et al., 2014) may also contribute to river base flow P concentrations, the role of soil processes and pathways to GW are also of concern. For example, research has highlighted the large proportion of stream water P associated with nanoparticles and colloids and that were assumed to come from soil colloids (Gottselig et al., 2017). Thus, it is important to improve the understanding of the drivers of P transfer from agricultural soils to GW to be able to mitigate eutrophication and improve stream water quality.

Soil chemistry and nutrient management of agricultural soils are varied and the components and forms of P present in animal slurry are different from those in synthetic inorganic fertilizers. It was assumed that aluminium (Al) and iron (Fe) rich soils would increase soil P_{coll} whereas animal slurry would decrease soil P_{coll}. The aim of this study was to understand the role of soil P_{coll} in the soil-water system and how this relates to mobilisation potential in groundwater-fed agricultural catchments. The major objective was to determine the influence of organic and synthetic P fertilizer on medium-sized soil P_{coll} and soluble soil solution P fractions using incubated soil samples and laboratory extractions.

2. Materials and methods

2.1. Sites description

Soils from three long-term agricultural catchment observatories in Ireland (Fealy et al., 2010; Shortle and Jordan, 2017; Wall et al., 2012) were used for this study, specifically Grassland A, Grassland B and Arable A. These catchments were chosen because they had some evidence of groundwater-fed streams to a greater (Arable A and Grassland A) and lesser degree (Grassland B) (Dupas et al., 2017; Mellander et al., 2016; Mellander et al., 2015). The catchments also varied in terms of land use, soil drainage class, soil type and chemistry and geology (SI 1). All three catchments have intensively farmed land with a range of bioavailable P concentrations (Morgan soil P test) in soils ranging from sub-optimum to excessive (Wall et al., 2012). Grassland A and Arable A have hillslope transects with piezometer nests for GW monitoring where soils were sampled for this study. Grassland B has a series of discrete GW monitoring points and soils close to two of these were sampled (SI 2).

2.2. Samples collection and pre-treatment

Soil sampling was conducted in 4 fields in Grassland A (downslope Gleysol (GA-1, GA-3) and midslope Cambisol/Podzol (GA-2, GA-4) soils), 2 fields in Grassland B (Planosol/Stagnosol (GB-5) and Cambisol/Leptosol (GB-6) soils), and 4 fields in Arable A (downslope Luvisol (AA-7, AA-9) and midslope Cambisol (AA-8, AA-10) soils) (SI 2) between January and March 2018 before fertilizer applications. Soil was sampled using a hand auger from 0 to 40 cm (Dupas et al., 2015) at several points along two W-shaped paths in an area of ca. 60 m^2 adjacent to the piezometer nests to get one composite soil sample for each site. The topsoil and the horizon below were mixed to account for attenuation processes once P_{coll} has been mobilised in the topsoil, important when assessing P_{coll} mobilisation potential to GW. In total, 10 composite soil samples were taken. All soil samples were air-dried (Dupas et al., 2015) and sieved to 12 mm to remove large stones and minimise soil aggregate destruction (De Boodt et al., 2013).

2.3. Treatments and incubation study

Before incubation, 5 treatments were applied on subsamples (triplicate, 150 g dry soil equivalent) of each of the 10 composite soil samples. The treatments included a control (C), a cattle slurry (0.29 kg P m^{-3}) treatment of 1.99 mg P kg^{-1} soil (CS1), a cattle slurry treatment of 3.99 mg P kg^{-1} soil (CS2), a synthetic fertilizer treatment (10–10–20 (N–P–K)) of 1.26 mg P kg^{-1} soil (SF1) and a synthetic fertilizer treatment (10—10—20) of 2.53 mg P kg^{-1} soil (SF2). The treatment types and application rates CS1 and SF1 were representative of the main farmers' practices in the catchments. Treatments CS2 and SF2 (double of CS1 and SF1) were used to assess the effect of application rate. The cattle slurry composition is shown in SI 3. In total, 150 soil subsamples were placed in 250 ml pots and incubated in a growth room in darkness with a bulk density of 1.2 g cm^{-3} (O'Flynn et al., 2018) at 15 °C for 8 weeks (Sarker et al., 2014). A 10 mm hole was drilled in the lids to maintain aerobic conditions. Soil moisture was kept at 70% of water-filled pore space (WFPS) by biweekly weighing each subsample and adding deionized water. Atmospheric humidity was kept between 70 and 80%. A complete flow chart of the methodology showing treatments, tests and abbreviations is shown in SI 4.

2.4. Chemical analysis

After incubation, all subsamples were centrifuged at 4500 rcf for 50 min to separate supernatants and soil cakes. Dilution factors ranging from 1.1 to 1.6 were applied to supernatants in order to provide enough soil solution for analysis. The supernatants were filtered using a 450 nm CA syringe filter (Sartorius) and analysed for dissolved reactive P (DRP_{ss}) by spectrophotometry after ascorbic acid reduction (MDL: 0.005 mg l^{-1}) (Askew and Smith, 2005). The soil cakes were then oven dried at 40 °C for 1 week and 2 mm sieved for further analysis (SI 4). A summary of abbreviations, descriptions and filtration sizes used for soil supernatants and colloidal extracts is presented in Table 1.

Table 1
Summary of abbreviations, descriptions and filtration sizes used for soil supernatants and soil colloidal extracts.

Abbreviation	Description and filtration size
Supernatant	**Soil solution separated from incubated soils by centrifugation and filtered at 450 nm**
DRP_{ss}	Soil solution dissolved reactive phosphorus
Water dispersible soil colloids	**Medium-sized soil colloids extracted with water from incubated soils and separated by membrane filtration (200–450 nm)**
TP_{coll}	Total colloidal phosphorus
RP_{coll}	Reactive colloidal phosphorus
UP_{coll}	Unreactive colloidal phosphorus, difference between total and reactive colloidal phosphorus
Al_{coll}, Fe_{coll}, Si_{coll}	Colloidal aluminium, colloidal iron, colloidal silicate
OC_{coll}	Colloidal organic carbon

2.4.1. Un-incubated bulk soil variability

The 10 un-incubated composite soil samples were characterised according to potential P_{coll} influences. For clay content, particle size distribution (PSD - sand, silt and clay content (%) (Brady and Weil, 2008)) were determined using the pipette method (Avery and Bascomb, 1974) and converted to textural classes (SI 4).

2.4.2. Incubated bulk soil variability

For the 150 incubated centrifuged soil cakes, the major soil P chemical precipitation/adsorption factors Al, Fe and calcium (Ca) were determined by Mehlich 3 extraction (Mehlich, 1984) in a 1:10 soil-to-Mehlich 3 reagent ratio for labile inorganic fractions determination. Mehlich 3 extractable P (M3-P), Al (M3-Al), Fe (M3-Fe) and Ca (M3-Ca) were measured by Varian VISTA Inductively coupled plasma-optical emission spectroscopy (ICP-OES - Varian, Palo Alto, CA). Total phosphorus (TP), aluminium (TAl), iron (TFe) and calcium (TCa) were similarly measured by ICP-OES after Nitric Acid (7.5 ml) and Hydrochloric Acid (2.5 ml) microwave digestion on 0.5 g soil samples (EPA 3052, 1996). Soil DPS (%) was calculated using the sum of M3-Al and M3-Fe as the denominator and M3-P as the numerator (Kovar and Pierzynski, 2009). Phosphorus sorption isotherms were also established in duplicate on the control (C) subsamples (using a composite sample of the triplicates) to note soil binding and P buffering characteristics following the technique of Pautler and Sims (2000). Two grams of soil were shaken (15 rpm) for 24 h with 30 ml of 6 P solutions ranging from 0 to 25 mg P l^{-1} (as KH_2PO_4). The suspensions were then filtered (Whatman filter paper no. 2) and analysed colorimetrically for reactive P (RP). The difference between P added in the initial solutions and P remaining in the filtrates was considered to have been sorbed. Maximum P sorption capacity (S_{max}) and P binding energy (k) were calculated using the Langmuir adsorption equation (Kovar and Pierzynski, 2009).

Soil pH was determined using a 1:2.5 soil-to-water ratio (Bryne, 1979). Organic matter content (OM%) was measured as the loss-on-ignition of 4 g samples at 500 °C (Storer, 1984). Blank and control samples were used in the extractions and P determination procedures to ensure analysis reliability (SI 4).

2.4.3. Incubated medium-sized soil colloids extraction and analysis

To examine the medium-sized colloidal fractions in each incubated soil cakes, Water Dispersible Colloids (WDCs) were extracted as they are easily dispersed from soil in contact with water (Rieckh et al., 2015) and have been suggested as model compounds for mobile soil colloids (Séquaris et al., 2013). Soil (20 g) was shaken (reciprocal shaker) with deionized water (1:8 soil-to-water ratio) for 24 h. The supernatant was then centrifuged at 3000 rcf for 10 min and filtered using a 450 nm CA membrane filter (Whatman) and a vacuum system. This is a modified procedure compared to Ilg et al. (2005) and Liu et al. (2014) to account for the dissolved P fraction, similar to the procedure for determining P in GW in the studied catchments and by consequence does not consider the larger colloidal fraction (>450 nm). Approximately half of the filtrate was then re-filtered using a 200 nm membrane filter and both filtrates were subsequently analysed for P_{coll} fractions and factors influencing P_{coll} binding (Fe and Al hydroxides, aluminosilicates, and OM). Total dissolved P (TDP) after alkaline persulphate oxidation (Askew, 2005) and, with DRP, after ascorbic acid reduction (MDL: 0.005 mg l^{-1}) (Askew and Smith, 2005) were analysed by spectrophotometry. Aluminium, Fe and silicate (Si) were analysed on a Varian Vista-MPX CCD-Simultaneous ICP-OES (IDL: 1 μg l^{-1}) (Gottler and Piwoni, 2005), dissolved organic carbon (OC) was analysed by a non-Diffractive Infra-Red (NDIR) detector after acidification and combustion (Baird, 2005). Medium-sized soil total P_{coll} (TP_{coll}), reactive P_{coll} (RP_{coll}), unreactive P_{coll} (UP_{coll}), and colloidal OC (OC_{coll}), Fe (Fe_{coll}), Al (Al_{coll}) and Si (Si_{coll}) were measured as the difference between their concentrations in the 200 nm unfiltered sample (<450 nm fraction) and the 200 nm filtered sample (<200 nm fraction) (SI 4, Table 1). Blank samples were used to ensure analysis reliability.

2.5. Statistical and data analysis

Pearson's correlation analysis was conducted to examine the relationship between medium-sized colloidal fractions, especially P_{coll}, and all PSD and chemical results from the un-incubated composite soil samples and the control (C) incubated soil cake samples, respectively, including the centrifuged supernatants DRP_{ss}. Significant correlation coefficients were determined at $P < 0.05$. A closer analysis was undertaken on the WDC fractions to test for significant correlations between these fractions.

To test for the significant effect ($P < 0.05$) of fertilizer application on soil M3-P, medium-sized soil P_{coll}, DPS and centrifuged supernatant DRP_{ss} fractions within and between each soil, ANOVA was conducted on chemical results from the control (C) and treated (CS1, CS2, SF1, SF2) incubated soil cakes samples and the centrifuged supernatants DRP_{ss}. Cattle slurry (CS1, CS2) and synthetic fertilizer (SF1, SF2) treatments were analysed separately as the application rates were different. Residuals plots were used to assess the normal distribution of the residuals and the equal variance of the data; data were log transformed before statistical analyses when those conditions were not met. To test for changes in the strength of factors influencing medium-sized soil P_{coll} and DRP_{ss}, Pearson's correlation analysis was conducted to examine the relationship between medium-sized colloidal fractions, especially P_{coll}, and all PSD and chemical results from the un-incubated composite soil samples and the treated (CS1, CS2, SF1, SF2) incubated soil cake samples, respectively, including the centrifuged supernatants DRP_{ss}.

All statistical analysis was carried out using R Studio version 3.5.2. Negative values in the WDC fractions due to a very small difference in concentrations between the two filtrates and/or concentrations below the detection limit or measurement error were counted as zero concentrations.

3. Results

3.1. Soils characteristics

3.1.1. Bulk soils

A summary of bulk soils characteristics is shown in Table 2. A correlation matrix between soil properties, P sorption parameters, DRP_{ss} and medium-sized colloidal fractions in untreated soils is also shown in Table 3. The Gleysol soils (GA-1, GA-3) showed the highest sand content (62%) whereas the Planosol/Stagnosol (GB-5) and Luvisol soils (AA-7, AA-9) showed the highest clay contents (26–28%). Concentrations of medium-sized RP_{coll} were positively correlated to clay content and, as expected, negatively correlated to sand content. Soil OM content ranged from 4.6% (Gleysol GA-3) to 8.3% (Cambisol/Podzol GA-4) and the range was too narrow to see any significant effect on medium-sized P_{coll}.

Table 2
Summary of untreated soils characteristics.

Site	Soil type (WRB)	Sand	Silt	Clay	Texture	pH	OM[a]	TAl[b]	TCa[c]	TFe[d]	TP[e]	M3-Al[f]	M3-Ca[g]	M3-Fe[h]	M3-P[i]	S_{max}[j]	k[k]	DPS[l]
		%	%	%			%	mg kg^{-1} soil	mg kg^{-1} soil	mg kg^{-1} soil	mg kg^{-1} soil	mg kg^{-1} soil	mg kg^{-1} soil	mg kg^{-1} soil	mg kg^{-1} soil	mg kg^{-1} soil	l mg^{-1}	%
GA-1	Gleysol	57	34	9	Sandy Loam	5.4	6.8	13411	1416	12499	505	1032	1000	352	61	714	2.33	4.4
GA-2	Cambisol/Podzol	47	36	17	Loam	6.3	7.8	14064	3433	19624	955	756	2170	254	45	714	1.40	4.4
GA-3	Gleysol	62	26	12	Sandy Loam	5.1	8.3	14876	1291	18488	602	818	917	261	90	714	1.17	8.3
GA-4	Cambisol/Podzol	46	37	17	Loam	5.6	4.6	13354	1180	25870	635	791	863	349	45	667	0.88	4.0
GB-5	Planosol/Stagnosol	44	28	28	Clay Loam	5.2	6.6	31667	2354	35366	895	938	848	213	2	909	15.71	0.1
GB-6	Cambisol/Leptosol	44	33	23	Loam	5.8	6.5	20096	2290	30860	1375	975	1339	250	90	833	1.33	7.4
AA-7	Luvisol	34	40	26	Loam	6.2	7.8	26707	2098	34703	924	922	1352	185	37	909	2.20	3.3
AA-8	Cambisol	38	39	23	Loam	6.1	7.3	23774	1621	33875	886	1017	1081	165	38	833	2.40	3.2
AA-9	Luvisol	38	35	27	Loam	5.9	7.3	24101	2069	32907	1042	978	1520	300	131	714	1.00	10.2
AA-10	Cambisol	38	37	25	Loam	7.0	6.6	30882	2700	36008	1100	1034	1778	171	56	833	3.00	4.6

[a] Soil organic matter.
[b] Total aluminium.
[c] Total calcium.
[d] Total iron.
[e] Total phosphorus.
[f] Mehlich 3 extractable aluminium.
[g] Mehlich 3 extractable calcium.
[h] Mehlich 3 extractable iron.
[i] Mehlich 3 extractable phosphorus.
[j] Maximum phosphorus sorption capacity.
[k] Phosphorus binding energy.
[l] Degree of phosphorus saturation.

Table 3
Pearson correlation matrix between soil properties, sorption parameters, soil solution dissolved reactive phosphorus and medium-sized soil colloidal fractions in untreated soils (n = 30). Significant correlations are shown in bold.

	Sand	Silt	Clay	pH	OM[a]	S_{max}[b]	k[c]	DPS[d]	TAl[e]	TCa[f]	TFe[g]	TP[h]	M3-Al[i]	M3-Ca[j]	M3-Fe[k]	M3-P[l]	DRP_{ss}[m]	TP_{coll}[n]	UP_{coll}[o]	RP_{coll}[p]	Al_{coll}[q]	Fe_{coll}[r]	Si_{coll}[s]
Sand																							
Silt	**−0.70**																						
Clay	**−0.86**	0.24																					
pH	**−0.66**	**0.73**	0.37																				
OM	0.11	−0.19	−0.01	0.06																			
S_{max}	**−0.56**	0.08	**0.71**	0.24	0.16																		
k	−0.07	−0.46	**0.42**	−0.32	−0.11	0.57																	
DPS	0.19	−0.12	**−0.17**	−0.02	0.28	−0.51	**−0.66**																
TAl	**−0.65**	0.08	**0.83**	0.36	0.09	**0.78**	**0.55**	−0.31															
TCa	−0.35	0.16	0.37	0.51	0.24	0.27	0.16	−0.12	0.29														
TFe	**−0.86**	0.31	**0.95**	**0.44**	−0.13	0.71	**0.34**	−0.20	**0.84**	0.22													
TP	−0.55	0.21	0.60	0.46	0.04	0.41	0.01	0.17	0.42	**0.72**	0.56												
M3-Al	−0.33	0.19	0.32	0.25	0.00	0.45	0.14	−0.02	**0.53**	−0.09	0.38	0.22											
M3-Ca	**−0.37**	0.43	0.19	**0.75**	0.33	−0.04	−0.32	0.21	0.07	**0.76**	0.08	0.46	−0.10										
M3-Fe	0.57	−0.20	−0.63	−0.53	−0.39	**−0.80**	−0.28	0.33	**−0.69**	−0.38	**−0.68**	−0.43	−0.27	−0.26									
M3-P	0.14	−0.09	−0.13	−0.02	0.21	−0.49	**−0.62**	**0.99**	−0.26	−0.14	−0.16	0.18	0.11	0.18	0.37								
DRP_{ss}	−0.20	−0.01	0.27	0.00	0.17	−0.27	**−0.30**	**0.79**	0.06	−0.03	0.18	0.26	0.16	0.18	0.23	**0.83**							
TP_{coll}	−0.09	0.21	−0.03	−0.01	**−0.52**	**−0.43**	**−0.27**	**0.25**	−0.21	−0.25	0.03	−0.07	−0.11	−0.11	0.46	0.28	0.37						
UP_{coll}	−0.04	0.18	−0.08	−0.04	**−0.53**	**−0.46**	**−0.24**	**0.20**	−0.25	−0.27	−0.02	−0.13	−0.17	−0.13	**0.48**	0.22	0.32	**0.99**					
RP_{coll}	**−0.45**	0.30	**0.39**	0.21	−0.07	0.14	−0.28	0.41	0.21	0.01	0.39	0.50	**0.42**	0.12	−0.06	0.47	0.46	0.25	0.13				
Al_{coll}	**−0.42**	**0.43**	**0.26**	0.36	−0.19	0.11	−0.23	0.07	0.20	0.07	**0.33**	0.27	0.15	0.16	−0.16	0.09	0.16	0.32	0.30	**0.35**			
Fe_{coll}	**−0.47**	**0.47**	**0.30**	0.41	−0.10	0.19	−0.22	0.03	0.25	0.08	**0.37**	0.25	0.20	0.17	−0.25	0.05	0.13	0.27	0.25	**0.34**	**0.96**		
Si_{coll}	**−0.42**	**0.39**	0.29	0.29	−0.18	0.10	−0.20	0.10	0.21	0.02	0.33	0.22	0.15	0.12	−0.11	0.13	0.23	0.31	0.29	**0.35**	**0.98**	**0.93**	

[a] Soil organic matter.
[b] Maximum phosphorus sorption capacity.
[c] Phosphorus binding energy.
[d] Degree of phosphorus saturation.
[e] Total aluminium.
[f] Total calcium.
[g] Total iron.
[h] Total phosphorus.
[i] Mehlich 3 extractable aluminium.
[j] Mehlich 3 extractable calcium.
[k] Mehlich 3 extractable iron.
[l] Mehlich 3 extractable phosphorus.
[m] Soil solution dissolved reactive phosphorus.
[n] Total colloidal phosphorus.
[o] Unreactive colloidal phosphorus.
[p] Reactive colloidal phosphorus.
[q] Colloidal aluminium.
[r] Colloidal iron.
[s] Colloidal silicate.

Soil TP content was the highest in the Cambisol/Leptosol soil (GB-6; 1375 mg kg^{-1} soil) and the lowest in Gleysol soils (GA-1, GA-3; 505–602 mg kg^{-1} soil). The highest TAl and TFe contents were measured in Planosol/Stagnosol (GB-5) and Cambisol (AA-10) soils whereas the lowest contents were measured in Gleysol (GA-1, GA-3) and Cambisol/Podzol (GA-2, GA-4) soils. Soil M3-P content was the highest in a Luvisol soil (AA-9; 131 mg kg^{-1} soil) and the lowest in the Planosol/Stagnosol soil (GB-5; 2 mg kg^{-1} soil). The highest M3-Al and M3-Fe contents were measured in Cambisol (AA-10) and Gleysol (GA-1) soils, respectively. The lowest M3-Al and M3-Fe contents were measured in Cambisol/Podzol (GA-2, GA-4) and Cambisol (AA-8, AA-10) soils, respectively. Soil M3-P was positively correlated to DRP_{ss} (R = 0.83). Soil M3-Al and M3-Fe contents were positively correlated to medium-sized RP_{coll} and UP_{coll} concentrations, respectively, as assumed.

Soil DPS was the highest in a Luvisol soil (AA-9; 10.2%) and the lowest in the Planosol/Stagnosol soil (GB-5; 0.1%). Soil DPS was positively correlated to DRP_{ss} (R = 0.79) and negatively correlated to k (R = −0.66).

Soil P sorption isotherms are shown in Fig. 1 and S_{max} and k values in Table 2. Maximum P sorption capacity S_{max} was the highest for Planosol/Stagnosol (GB-5) and Luvisol (AA-7) soils (909 mg P kg^{-1} soil) and the lowest for a Cambisol/Podzol soil (GA-4; 667 mg P kg^{-1} soil). Soil P binding energy k was the lowest for Cambisol/Podzol (GA-4) and Luvisol (AA-9) soils (0.88–1.00 l mg^{-1}) and the highest for the Planosol/Stagnosol soil (GB-5; 3.00 l mg^{-1}). Soil S_{max} was negatively correlated to medium-sized TP_{coll} and $UP_{coll.}$ Soil k and especially S_{max} were positively correlated to clay content and TAl content. Soil S_{max} and k were also negatively correlated to M3-Fe and M3-P, respectively.

3.1.2. Medium-sized soil colloids and soil solution

Medium-sized P_{coll} and colloidal metal (Al, Fe, Si) concentrations across the 10 sites are shown in Fig. 2 and correlations between medium-sized colloidal fractions are shown in Table 3. Concentrations of OC_{coll} are not shown as results were all negative and assumed to be due to too small a difference in concentrations leading to measurements below the detection limit or measurement error. This may indicate that P_{coll} was not associated with OM in the medium-sized colloidal fraction. Concentrations of medium-sized TP_{coll}, UP_{coll} and RP_{coll} ranged from 0.000 to 0.046 mg l^{-1}, from 0.000 to 0.045 mg l^{-1} and from 0.000 to 0.007 mg l^{-1}, respectively. The highest medium-sized TP_{coll} and UP_{coll} concentrations were measured in Cambisol/Podzol (GA-4) and to a less extent in Luvisol (AA-9) soils where UP_{coll} concentrations were variable. The lowest medium-sized TP_{coll} and UP_{coll} concentrations were measured in the Planosol/Stagnosol soil (GB-5). Concentrations of medium-sized TP_{coll} and UP_{coll} were very strongly correlated (R = 0.99). The highest values of medium-sized Al_{coll}, Fe_{coll} and Si_{coll} concentrations were recorded in Luvisol (AA-7, AA-9), Cambisol (AA-8, AA-10) and Cambisol/Leptosol (GB-6) soils but also in a Cambisol/Podzol (GA-4) soil. However, concentrations were variable for all these sites. Concentrations of medium-sized Al_{coll} and Fe_{coll} were very strongly correlated with each other (R = 0.96), as were medium-sized Al_{coll} and Si_{coll} concentrations (R = 0.98) and medium-sized Fe_{coll} and Si_{coll} concentrations (R = 0.93). Only medium-sized RP_{coll} concentrations were positively but moderately correlated to medium-sized Al_{coll}, Fe_{coll} and Si_{coll} concentrations.

Concentrations of DRP_{ss} are also shown in Fig. 2 and ranged from 0.006 to 0.134 mg l^{-1}. The highest and lowest concentrations were measured in a Luvisol soil (AA-9) and in the Planosol/Stagnosol soil (GB-5), respectively.

3.2. Treated soils phosphorus fractions

3.2.1. Bulk soil phosphorus

For the cattle slurry treatment, ANOVA showed an increase in the labile inorganic P pool (i.e. M3-P) in soil AA-8 after CS1, in soils GA-1, GA-2 and GA-3 after CS2 and in soil GA-4 after CS1 and CS2 treatments (with no difference between CS1 and CS2). The synthetic fertilizer treatment had no effect on soil M3-P. In treated soils (n = 120), M3-P and DPS were strongly correlated to DRP_{ss} (R = 0.83 and 0.80, respectively).

3.2.2. Medium-sized soil colloids and soil solution phosphorus

Concentrations of medium-sized UP_{coll} were not influenced by any of the P treatments (Fig. 3). However, medium-sized RP_{coll} concentrations decreased by 0.005 mg P l^{-1} in Luvisol soil AA-9 (with no variation in soil DPS) and increased by 0.011 mg P l^{-1} in Cambisol/Podzol soil GA-4 after SF2 (synthetic fertilizer 2.53 mg P kg^{-1} soil, 12.1 kg P ha^{-1}) treatment (also compared to SF1) (Fig. 3) as was soil DPS. Increase in medium-sized TP_{coll} concentrations (0.005 mg P l^{-1}) between SF1 and SF2 treatments in Gleysol soil GA-1 was not associated with variation in soil DPS. A DRP_{ss} increase of 0.021 mg P l^{-1} was also measured in Cambisol/Leptosol soil GB-6 after SF2 treatment with no change in soil DPS. Application of SF1 (synthetic fertilizer 1.26 mg P kg^{-1} soil), CS1 and CS2 (cattle slurry 1.99 and 3.99 mg P kg^{-1} soil, respectively) treatments did not affect medium-sized P_{coll} concentrations even though DPS increased in some soils after CS1 (GA-4) and CS2 (GA-1, GA-3, GA-4, GB-6) treatments. However, DRP_{ss} increased after CS1 and CS2 treatments (0.008 and 0.013 mg P l^{-1}, respectively) in Cambisol/Podzol soil GA-4 as was soil DPS. Even at a higher application rate than the synthetic fertilizer treatment (SF2), the cattle slurry treatment (CS2) did not influence medium-sized P_{coll} concentrations. However, concentrations were variable in GA-4, AA-9 and to a lesser extent GB-6 soils.

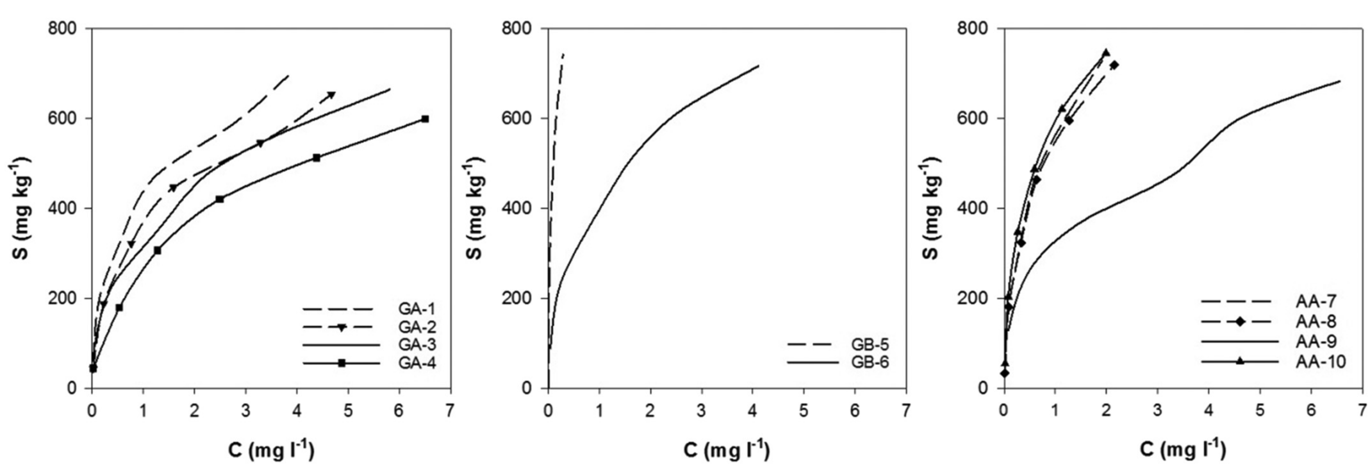

Fig. 1. Phosphorus sorption isotherms of the untreated soils in left) Grassland A catchment, middle) Grassland B catchment and right) Arable A catchment. Soils within the same hillslope are presented with the same line style (solid or dash), soils at midslope are presented with symbols. All measurements were conducted in duplicate.

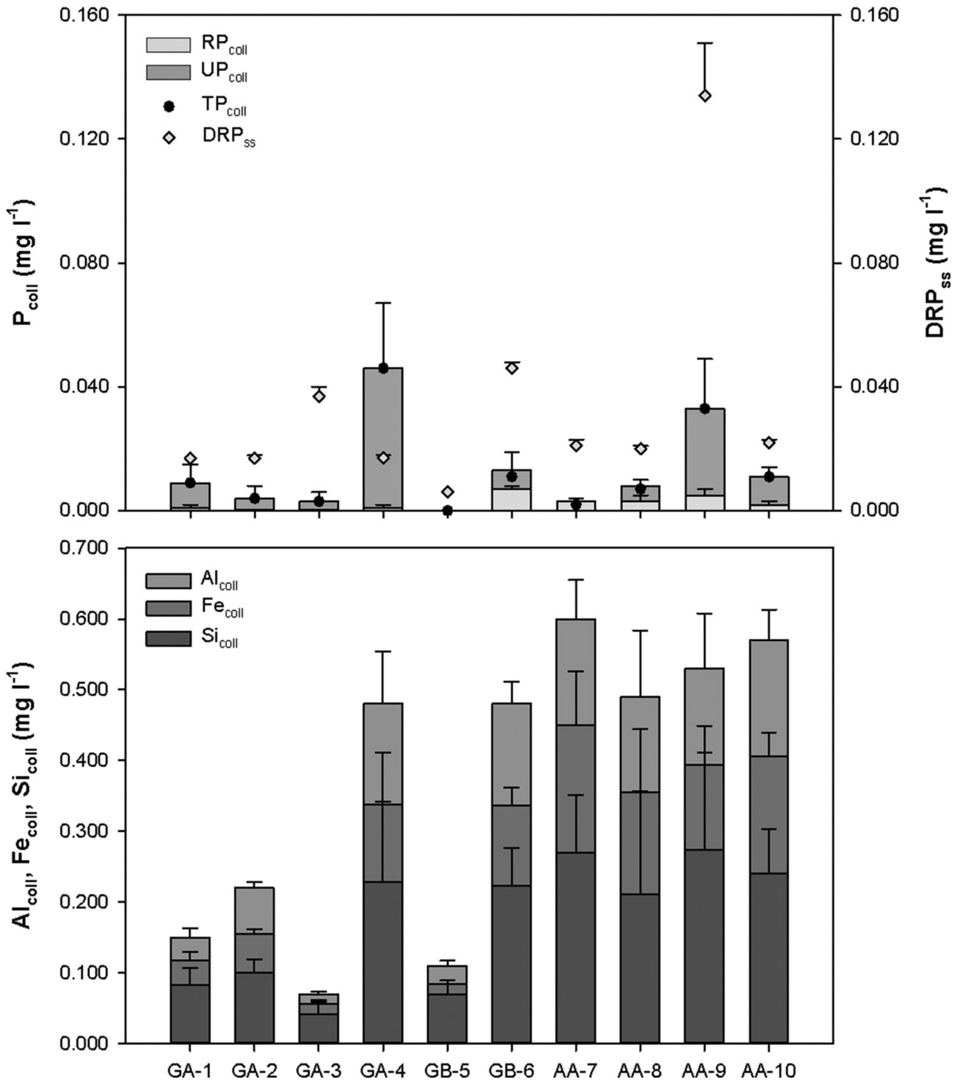

Fig. 2. top) Total (TP_{coll}), reactive (RP_{coll}) and unreactive phosphorus (UP_{coll}) average concentrations (±SE) in medium-sized (200–450 nm) soil Water Dispersible Colloidal fraction and soil solution DRP (DRP_{ss}) average concentrations (±SE) in untreated soil samples. Reactive and unreactive fractions are presented as stacked bars and total fraction is presented as black dots. Standard error bars shown only for reactive and unreactive fractions. Soil solution DRP is presented as grey diamonds; below) Colloidal metals (Al_{coll}, Fe_{coll}, Si_{coll}) average concentrations (±SE) in medium-sized (200–450 nm) soil Water Dispersible Colloidal fraction in untreated soil samples. All measurements were conducted in triplicate.

After P application, medium-sized TP_{coll} and UP_{coll} remained strongly correlated with each other (R = 0.98) as were medium-sized colloidal metals (Al, Fe, Si) (R = 0.99).

4. Discussion

This study assessed the role of soil physical and chemical properties and P fertilization practices on soluble P and medium-sized P_{coll} concentrations in contrasting agricultural soils and the implications for leaching of P_{coll} to GW.

4.1. Influence of soil properties on medium-sized colloidal phosphorus

Colloidal P concentrations differed between untreated soils and medium-sized P_{coll} was mostly composed of unreactive P associated to amorphous forms of Fe. Previous studies also demonstrated that especially organic P (part of the unreactive fraction) was associated with WDCs (Jiang et al., 2015; Missong et al., 2016). As initially assumed, soil M3-Fe and M3-Al increased unreactive and reactive medium-sized P_{coll}, respectively. The strong correlation found between medium-sized colloidal metals (Al, Fe and Si) suggested the presence of clay minerals such as phyllosilicate, as found by Missong et al., (2018a) in the medium-sized colloidal fraction, and sesquioxides of Fe and Al.

Soil M3-Fe, DPS and sorption parameters (S_{max} and k) appeared to be the main controlling factors of medium-sized P_{coll} mobilisation and soluble P concentrations. Higher medium-sized TP_{coll} and UP_{coll} concentrations were associated with higher soil M3-Fe content and lower soil S_{max} and k whereas lower medium-sized TP_{coll} and UP_{coll} concentrations were associated with higher S_{max}, k and lower DPS. Higher soluble P concentrations, that include in part medium-sized P_{coll}, were also associated with higher soil DPS. Evidence of the effect of high P saturation on the dispersion of colloid-bound P due to more mobilisation and higher P content (Ilg et al., 2005) has been previously supported by Siemens et al. (2004) and Ilg et al. (2008). High soil S_{max} also appeared to decrease medium-sized P_{coll} mobilisation and was here positively correlated to soil TAl and clay contents. Higher mobilisation of medium-sized P_{coll} in the Cambisol/Podzol soil (GA-4) could be related to the high mobility of OM-Fe associations and supports previous findings of Missong et al. (2018b) on the dominance of OM in leached colloids. Moreover, low medium-sized P_{coll} concentrations measured in the soil with the highest OM content (GA-3) could possibly indicate that P_{coll} may mainly be in the fine colloidal and nanoparticulate fractions (<200 nm) (not studied here), richer in OM as suggested by Missong et al. (2018a). Results may

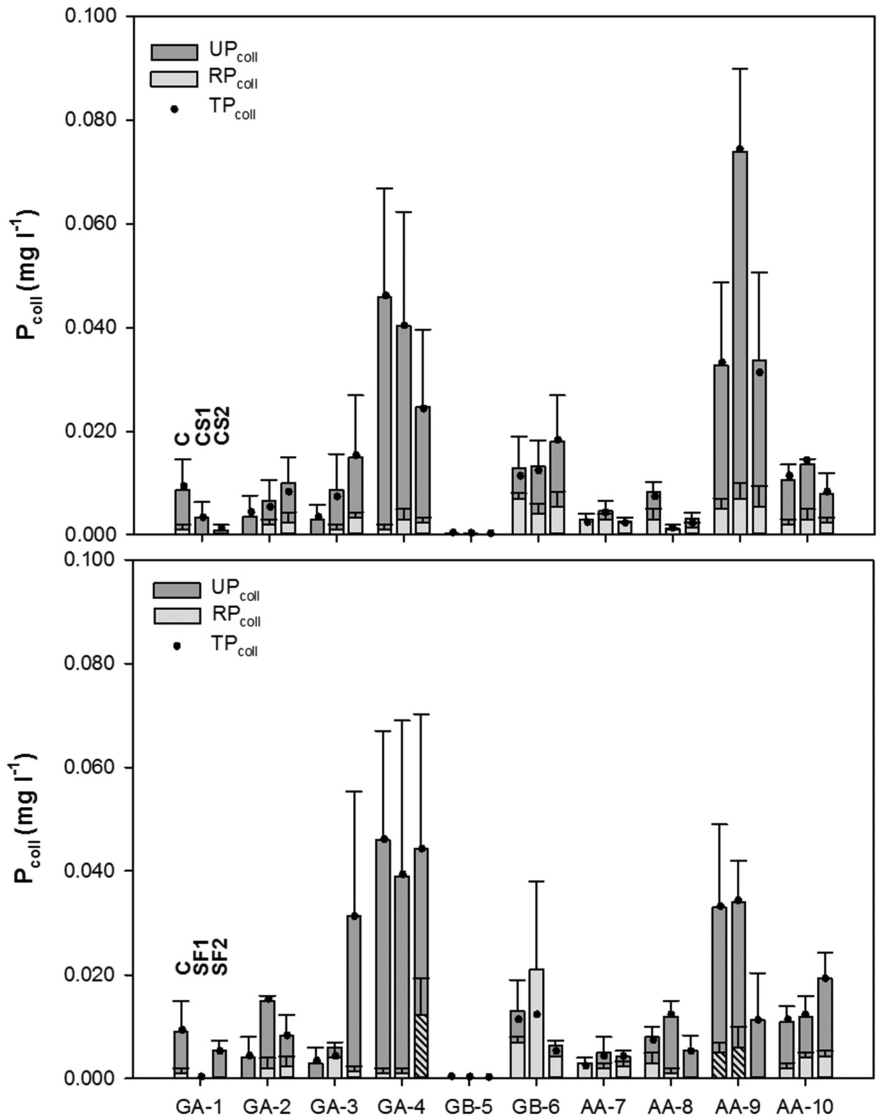

Fig. 3. Total (TP_{coll}), reactive (RP_{coll}) and unreactive phosphorus (UP_{coll}) average concentrations (±SE) in medium-sized (200–450 nm) soil Water Dispersible Colloidal fraction in incubated soil samples after top) cattle slurry (CS1 and CS2) and below) synthetic fertilizer (SF1 and SF2) treatments. Reactive and unreactive fractions are presented as stacked bars and total fraction is presented as black dots. Standard error bars shown only for reactive and unreactive fractions. Significant difference ($P < 0.05$) between control (C) and treatments (CS1 or CS2, SF1 or SF2) or between treatment application rates within each site are shown with diagonals. All measurements were conducted in triplicate.

indicate that background soil OM content attenuate medium-sized P_{coll}, as suggested in previous studies where P adsorption by Fe oxides was reduced in the presence of organic compounds (Yan et al., 2016), but the range of OM content in this study was too narrow (4–9%) to strongly support this hypothesis.

Colloidal-P binding materials and relationships with soil properties, soil DPS and P sorption parameters vary regarding the size of the colloidal fraction (Missong et al., 2018a). The medium-sized (200–450 nm) colloidal fraction considered in this study does cover a quarter of the entire colloidal fraction (1–1000 nm). Therefore, some colloidal properties such as high specific binding for P are likely to be much lower in the medium-sized colloidal fraction than in the finer colloidal and nanoparticulate fractions (<200 nm). Hence, the results here possibly underestimate the complete role of P_{coll} in mobilisation processes and further work would be needed to look at the finer colloidal and nanoparticulate fractions in the <200 nm range (Missong et al., 2018a; Gottselig et al., 2017).

4.2. Impact of fertilization practices on medium-sized colloidal phosphorus

Medium-sized P_{coll} mobilisation and soluble P concentrations appeared to be controlled differently regarding the P treatment type (organic, synthetic). Medium-sized P_{coll} concentrations were only influenced by the synthetic fertilizer treatment (SF2 only), even at a lower application rate compared to cattle slurry, while DRP_{ss} concentrations were increased by both types of treatments. Hence, the cattle slurry treatment did not decrease medium-sized P_{coll}, as assumed, and had no effect.

The results suggest that application of cattle slurry (and associated organic anions) may reduce the sorption sites available for P by competition, as shown in previous studies (Oburger et al., 2011). However, it may as a consequence increase soil DPS and DRP_{ss} concentrations (bioavailable) especially in soils with low S_{max} and k as measured in GA-4. Soil DPS appeared to be a key parameter controlling DRP_{ss} concentrations in treated soils and is known to enhance the dispersion of colloid-bound P (Siemens et al., 2004; Ilg et al., 2008). On the other hand, contrasting (increase and decrease) effects of the synthetic fertilizer treatment on medium-sized RP_{coll} concentrations (GA-4 and AA-9, respectively) also support the key role of soil DPS. Application of P to soils with higher DPS may destabilise the previously adsorbed P (this may require further investigation as no significant increase in DRP_{ss} was measured) whereas in soils with lower DPS it may promote binding of P (as suggested by the increase in DPS).

However, the effect of one single fertilizer application on soluble P and P_{coll} doesn't take into account the temporal variation due to several P applications. Parameters such as DPS, S_{max} and k would likely be modified and be responsible for increasing soluble and P_{coll} concentrations. Further work would be needed to assess the temporal changes of P saturation and sorption using multiple P applications and to assess their importance for P_{coll} mobilisation over time (existence of a tipping point). Hence, the lack of response for some soils may be related to soils far from P saturation. Moreover, the significant variation between the sample replicates (especially for medium-sized UP_{coll}) in treated and untreated soils (especially for GA-4 and AA-9 with the highest medium-sized P_{coll} concentrations) indicates the difficulties to precisely assess P_{coll} and the limitation of the filtration technique used (Zirkler et al., 2012). However, this still shows the higher potential for medium-sized P_{coll} in these soils but can also be responsible for the lack of variation measured between treatment application rates.

4.3. Implications for losses of soil colloidal phosphorus to transfer pathways to groundwater

A soil chemical assessment is required to consider the roles of medium-sized P_{coll} processes using results from this study. Soil chemical properties as M3-Fe, DPS and S_{max} are important for mitigating medium-sized P_{coll} (which is mainly unreactive P) concentrations mobilised in soils and reduce P losses to GW and surface water. In these water bodies, medium-sized P_{coll} can become bioavailable after P release (Jeanneau et al., 2014; Lambert et al., 2013; Montalvo et al., 2015) and cause ecological issues. However, soil chemical properties can be variable in space and specific soil tests are required to localise critical areas where risks of P_{coll} mobilisation are important with an emphasis on metals contents (especially Fe) and DPS. Hence, frequent soil P tests are needed in order to more carefully manage high P soils with more adapted P fertilization types/rates/fractionations. As cattle slurry treatment did not indicate any effect on medium-sized P_{coll} concentrations, even at a higher application rate than synthetic fertilizer, use of this type of fertilizer, especially in soils with higher M3-Fe and DPS, would attenuate medium-sized P_{coll} that could potentially be mobilised and lost to GW. However, the data here suggest that there is likely to be an increase in DRP_{ss}, or at least associated with colloids or nanoparticles less than 450 nm. This will require further investigation. These last two points on the association between soil P_{coll} and DRP_{ss} is important as P_{coll} can be readily mobilised and easily lost to GW, i.e. some P_{coll} forms may be bioavailable (Van Moorleghem et al., 2013), whereas DRP_{ss} is considered directly plant available.

Further to these soil chemistry considerations for mobilisation, P_{coll} can be leached to GW via macropores or preferential flow paths (Bol et al., 2016; Julich et al., 2017) especially in grassland catchments that tend to have more macropore pathways (Kramers et al., 2012) and may be enhanced by soil cracking during droughts. Further research is, therefore, required to understand the role of soil physical properties on P_{coll} transfer to GW and, at larger scales, investigations on the role of P_{coll} in the delivery of P to surface water are needed. This will add important insights into the particulate to dissolved P concentration spectrum in the soil-water environment, including colloids and nanoparticles, to better understand mobilisation and pathways, and their spatial and temporal dynamics.

5. Conclusion

This study investigated medium-sized soil P_{coll} (200–450 nm) and soil solution soluble P (<450 nm) fractions in contrasting untreated soils and the influence of organic and synthetic fertilizer P treatments to provide a chemical risk assessment of medium-sized P_{coll} mobilisation to GW. Soil WDC P and P-binding materials were analysed along with soil solution soluble P. The study highlighted an effect of soil properties on medium-sized soil P_{coll} mobilisation and its association with soluble P. Soil M3-Fe and M3-Al positively influenced medium-sized unreactive and reactive P_{coll}, respectively. In P treated soils, application of organic P had no effect on medium-sized P_{coll} even at a higher rate of application than the synthetic fertilizer treatment. However in soils with low P sorption properties, it may increase soil DPS and soluble P, important for plant uptake.

Results of the present study have important implications for localisation of soils with high potential for medium-sized P_{coll} (and other colloidal fractions) mobilisation/attenuation. Additional soil parameters should be integrated in soil testing and include metal contents (M3-Fe and M3-Al) and DPS measurements with frequent soil P tests (M3-P). This is especially important for catchments or fields with Cambisol/Podzol soils. Furthermore, the association between soil P_{coll} and soil solution P is important and has to be further investigated to optimise plant uptake and reduce environmental risk of P leaching to GW.

CRediT authorship contribution statement

Maelle Fresne: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Phil Jordan:** Conceptualization, Methodology, Writing - review & editing. **Owen Fenton:** Conceptualization, Methodology, Writing - review & editing. **Per-Erik Mellander:** Conceptualization, Methodology, Resources, Writing - review & editing, Funding acquisition. **Karen Daly:** Conceptualization, Methodology, Validation, Resources, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary informations

Catchments characteristics are presented in SI 1, soil sampling locations in the study catchments are shown in SI 2, cattle slurry chemical composition is presented in SI 3, and flow chart of the methodology is shown in SI 4. Supplementary informations to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142112.

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